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(54) Name of Invention: Resin composition for optical disc substrate

(57) Abstract:
Purpose: To produce the titled composition which transmits laser light sufficiently, adheres well to an inorganic thin film formed thereon as an information recording layer, and has excellent heat resistance when used in a magneto-optical disc utilizing magnetic change or in a phase-change optical disc.
Constitution: The titled composition is obtained by compounding 100 pts.wt. matrix resin (e.g. a polycarbonate resin or an amorphous polyolefin resin) with 5-100 pts.wt. silicone oxide powder having a particle diameter of 2-100nm.

Claims

What we claim is:

1. Resin composition for an optical disc substrate that compounds 100 pts.wt. matrix resin (e.g. a polycarbonate resin or an amorphous polyolefin resin) with 5-100 pts.wt. silicone oxide powder having a particle diameter of 2-100nm when used in a resin composition for an optical disc substrate that enables optical writing or re-writing of recorded information.
2. Resin composition for an optical disc substrate, as claimed in claim 1, where the matrix resin is a polycarbonate resin.
3. Resin composition for an optical disc substrate, as claimed in claim 1, where the matrix resin is an amorphous polyolefin resin.

Description

Background of the invention:

This invention relates to a resin composition for a phase-change optical disc substrate which enables optical writing or re-writing of recorded information, and in particular, a resin composition which can manufacture a substrate that transmits laser light sufficiently, adheres well to an

inorganic film when used in a magneto-optical disc utilizing magnetic change or in a phase-change optical disc.

Traditional technology:

Because of its credibility in informational record, excellent access rate, record storage, storage capacity, magnetic recording, such as in a magnetic floppy disc and in a magnetic hard disc, is often used as an informational record method, including in the external storage of computers.

On one hand, because of its ability for high-density informational record, the optical recording method has been put into practical use as a data storage medium. The fundamental structure of a disc used in this method, which laminates inorganic thin films for recording upon transparent media, enables it to have an excellent storage capacity which cannot be achieved by a magnetic recording method.

An inorganic glass or transparent resin is used as a material for the substrate, because the material for an optical disc requires high transparency to laser light for transmittance through the disc.

A polycarbonate resin is often used as a transparent resin. Composite polymers with polystyrene are also considered to overcome the fact that polycarbonate resins may cause birefringence after molding. Amorphous polyolefin resins are also used. ('Plastic, 41, p81-85, 1990, JP Patent 2-133413)

Aim of this Invention:

Polycarbonates have an excellent workability and mechanical properties as compared to other transparent resins, but on the other hand, easily cause birefringence when compared to glass, and have poor heat resistance, water absorption resistance and reliability of data saving. The largest problems are birefringence and water absorption resistance. Birefringence leads to reading errors because of the lack of clarity of the recorded information. Polycarbonates have a relatively low water absorption rate (0.2-0.3%) therefore do not cause a decrease in the physical and optical properties. However components of recording thin layers such as rare metals (terbium, gadolinium) induce corrosion and degradation because of the small amounts of water, cause insufficiency of information recording and disappearance of information during saving. Further, they induce frequent bit error rates caused by the insufficient adhesion to the inorganic thin layers that are formed as recording thin layer components. They even induce spalling or

cracks in the inorganic thin layer over time, high temperature or high humidity conditions. Therefore it is required to decrease water absorption.

On the other hand, amorphous polyolefin resins have lower water absorption rates and birefringence but have the same problem as polycarbonate resins of adhesion to inorganic thin layers. Glass substrates have excellent reliability but have bad workability and require high cost. Some technologies have been developed to solve these difficulties, but none of them are sufficient. A method of improving adhesion of the resin substrate to the inorganic thin layer, while improving adhesion, still retains the difficulties in post-processing viz. of the removal of deformation caused by the stress during the adhesion improvement process.
This invention focuses on these difficulties. Therefore the aim of this invention would be to provide a resin composition for an optical disc substrate that has excellent transparency, water adsorption resistance, adhesiveness to an inorganic thin layer and workability for formation.

Method to solve the difficulties:
This resin composition of an optical disc that enables optically written and re-written recording information containing 5-100 g silicone oxide powder with a particle diameter of 2-100 nm (relative to 100 g matrix resin)

Function:
First, the matrix resin used in this invention will be explained. Any matrix resin can be utilized as long as they have excellent optical and physicochemical properties. Among those resins, polycarbonate resins have well-balanced properties. The preferred viscosity-average molecular weight is 1,000-100,000, preferably 10,000-30,000. Products with low molecular weights tend to be fragile, while those with high molecular weights have low fluidity and ability of formation; therefore these are not suitable as a substrate for an optical disc. Blend resins of polycarbonate with polystyrene or ABS resins are also usable as long as they contain sufficient compatibility and affinity with silicone oxide powder. Amorphous polyolefin resins are also usable.
A preferred silicone oxide powder is silica sol which is obtained by aerial oxidation of silicon or neutralization, evaporation and particle growth of silicate glass in solvent. The transparent resin composition is obtained by dispersing particles in a matrix resin during second aggregation.

Because the surface of the aerially oxidized silicon powder is hydrophobic, it disperses in the matrix resin and provides a resin composition with excellent transparency. On the contrary, the surface of silicone oxide powder obtained by water-based sol tends to have hydroxyl or ionized

groups, and is therefore difficult to disperse in the matrix resin due to low compatibility. In such cases it is required to hydrophobize the surface of sol particle by a silicon compound.

Aerially oxidized silicon powder is commercialized by Aerosil (Aerosil, Japan) and easily obtained. Silica sols that disperse in water or organic solvent are also common. Methanol silica sol (Nissan chemicals) and Oskal1232 (Catalysts & Chemicals Industries Co., Ltd.) are commercially available.

The oxidized silicon powder stated above has to have a particle diameter of 2-10 nm; small particles (less than 2 nm) confer low water resistance and humidity resistance to the product resin, while large particles (>100 nm) not only cause lower transparency resin compositions but also increase the error rate caused by smoothness of surface, and are therefore inadequate as substrates for optical discs.

In order to improve the compatibility and dispersibility with the matrix resin, it is useful to hydrophobize the surface. These powders are commercially available (toluene sol). It should be noted that some of them are able to mix with the matrix resin without any surface hydrophobization depending on the formation conditions of the silicon oxide powder, type of matrix resin and the blend procedures employed.

There are no limitations on the manner of blending the matrix resin with the silicon oxide powder hence either the regular method or modified method can be employed. A typical method would be as follows: (1) Add silicon oxide powder into the melting matrix resin. Inject it into a mold after mixing thoroughly. (This method can be used for solid powders of silica oxide). (2) Disperse or dissolve the matrix resin in an organic solvent, add silica sol or silica oxide powder and mix the components. (3) Dissolve matrix resin into a dispersed medium of silica sol.

The composition ratio of the matrix resin to the silicone oxide powder cannot be fixed since it depends on the type of matrix resin and silicone oxide powder, blend conditions employed and the required properties of the substrate (e.g. mechanical properties, heat resistance). However it is required to contain between 5-100 g (preferably 7-50g) silicone oxide powder in 100 g matrix resin to retain its property as a substrate for an optical disc. A shortage of silicone oxide powder causes low adhesiveness to the inorganic thin layer. On the contrary, an excess of silicone oxide powder causes a decrease in elasticity and mechanical breaking strength. Both conditions results in poor substrate properties.

The adequate component composition is as stated above. It is also possible to add antioxidants or stabilizing materials, if necessary, to remove low molecular weight materials, oligomers and residual organic solvents in the matrix resins for certain compositions.

The resin composition used in this invention has to have sufficient transparency as a substrate, that is, it is preferred that the disc substrate (thickness 1.2 mm) has a light transmittance of 80 % and Haze (which indicates the rate of scattered light as noise among the transmitted light) of 10 % (less than 5 % is preferred). It is preferred to control the particle diameter, blending quantity and dispersion condition of the silicone oxide powder in order to satisfy these requirements.

Haze is calculated as below.

$H = (T_d/T_t)*100$ (%)

Where T_t is the light transmittance and T_d is the diffuse transmittance rate as measured the by the scattered light amount and transmitted light amount through the test substrate as explained in JIS K7105, special optical property section.

Light transmittance is preferred to be above 80 %; however this condition is usually satisfied as long as Haze is below 10 % when optical grade polycarbonate resins or amorphous polyolefin resins are used as the matrix resin. However it should be noted that light transmittance goes under 80 % when modified polycarbonate resins and amorphous polyolefin resins are used.

The resin compositions stated above form pellets using pressing machines and disc substrates by injection using stumpers.

The common procedure for the formation of the recording thin layers on a substrate is as mentioned above. For example, the formation of the recording thin layer is completed by creating a dielectric layer of silicone nitride and oxidized nitrogen and alloy metals such as Tb, Fe, Co, Gd and Nd by spattering, and a reflective layer of Aluminum or Aluminum nitride.

Generally, annealing is completed before the formation of the thin layer explained above. By using the resin composition in this invention, vacuum conditions are reached at relatively mild annealing conditions as compared to the case where the substrate consists of only matrix resins.

This invention not only improves the heat resistance and water absorption resistance of the compounded materials by dispersing silicone oxide powder in the matrix resin but also the chemical stability and adhesiveness of inorganic thin layer to the silicone oxide powder,

dispersed in the resin, exposed by surface activation via spattering during the formation of the thin layer laminated on the silicon oxide powder.

Examples of the present invention and comparison examples are given below, but these examples by no means restrict the invention:

Example 1: 100 g of polycarbonate resin palates with a viscosity-average molecular weight of 20,000 was dissolved in dichloromethane. To the solution 50 g of silicone oxide powder having a particle diameter of 16 nm (Aerosil 130, AEROSIL®, Japan) was added. The suspension was kneaded and dispersed. Dichloromethane was removed under reduced pressure and a crude resin composition was obtained. The obtained composition was palletized using a press machine and a magneto-optical disc substrate (diameter: 130 mm, thickness: 1.2mm) was formed using an injection machine.

The formed substrate was set onto a sputtering apparatus, annealed for 30 minutes at 90 °C in vacuum, a high-frequency electric field with flowing of Argon and oxygen (1:1) was applied, and plasma processing was carried out for 10 minutes. Magneto-optical discs were obtained by coating the plasma processed surface with a silicone nitride layer (thickness: 0.1 um), a Tb/Fe/Co metal layer (0.1um), a silicon nitride layer (0.1 um) and an aluminum layer (0.1 um) as the reflection layer by sputtering method. Table 2 shows the properties of the obtained disc. The properties were analyzed by the method explained below.

Haze: Haze was measured by using a Haze meter (No 206, Toyo Kiki, Japan)

Adhesiveness: A thin layer disc was first left for 500 hours at 80 °C, 90 % humidity and a cross cut tape test was applied. That is, 100 squares (1 mm^3) was formed onto the test product, adhesive tape was attached and detached vertically. The condition of thin layer on the surface of the product was examined, and the adhesiveness was expressed by the number of squared left.

Heat resistance: A thin layer disc was left for 500 hours at 80 °C, 90 % humidity, and the existence of surface pinholes was examined by optical microscope and polarization microscopy. Surfaces without dramatic change were considered as good surfaces.

Reliability: A thin layer disc was left for 500 hours at 80 °C, 90 % humidity, and the bit error rate before and after the test was measured. Discs with a value of $5*10^{-5}$ were considered as good surfaces.

Birefringence: measured by an ellipsometer (wave length: 630 nm)

Linear coefficient of expansion: The average of the linear expansion coefficients for a range of temperatures from room temperature to 100 °C was measured using a test piece (1.2 mm).
Water absorption: measured by the weight difference in a test piece (1.2 mm) before and after water soaking for 48 hours.

Example 2-6: The procedures of Example 1 were repeated only changing the diameter and amount of silicone oxide powder used as shown in Table 1. The results are shown In Table 2

Example 7: The procedures of Example 1 were repeated using amorphous polyolefin resin instead of polycarbonate resin, and adding cyclohexane as the fluxing material. The results are shown in Table 2.

Example 8: The procedures of Example 1 were repeated using colloidal silica instead of silicone oxide powder. That is, 100 g of polycarbonate resin palates were dissolved in dichloromethane. To the solution 160 g of colloidal silica dispersed in toluene (concentration of solid 30 wt%, particle diameter 20 nm) was added with stirring. The solvent was removed with stirring and a crude resin was obtained. The solvent was further removed by heating and the obtained composition was palletized using a press machine and the magneto-optical disc substrate was formed using an injection machine. The properties of the substrate were analyzed with the same procedures as Example 1. The results indicate that the material has excellent properties as a magneto-optical disc as shown in Table 2.

Example 9: The procedures of Example 8 were repeated using amorphous polyolefin instead of polycarbonate resin, and adding cyclohexane as the fluxing material. The results are shown in Table 2. It confirms the excellent properties and reliability of the material as a disc substrate.

Comparison Example 1: The procedures of Example 1 were repeated except for the abbreviation of the silicone oxide powder and plasma processing. The obtained disc caused partial spalling of the thin layer during the permanence test in high humidity conditions and a local defect during the bit error rate test.

Comparison Example 2: The procedures of Example 1 were repeated using 3 g of silicone oxide powder instead of the amount stated in Example 1. The effect of addition of silicone oxide powder was not detected and the same defects as Comparison Example 1 were confirmed.

Comparison Example 3: The procedures of Example 1 were repeated using 150 g of silicone oxide powder instead of the amount stated in Example 1. The obtained substrate was fragile and small cracks were confirmed after formation of the thin layer, therefore it was unusable.

Comparison Example 4: The procedures of Example 1 were repeated using silicon oxide powder with average particle diameter of 2 nm instead of the amount stated in Example 1. The bit error rate of this magneto-optic disc increased constantly and reached 10^4 in a short time in high humidity condition over the reliability test.

Comparison Example 5: The procedures of Example 1 were repeated using silicon oxide powder with average particle diameter of 200 nm instead of the amount stated in Example 1. The obtained disc possessed a large turbidity (15 % Haze) and low transparency.

Table 1:

Example	Polycarbonate (g)	Silicone oxide powder	
		Particle diameter (nm)	Amount (g)
2	100	16	5
3		16	25
4		16	75
5		16	100
6		7	50

Table 2:

Example	Haze (%)	Light transmittance	Adhesiveness	Heat resistance (existence of pin hole)	Reliability (increase in BER)	Birefringence (nm)	Linear coefficient of expansion ($10^{-5}deg^{-1}$)	Water absorption (%)
1	5.5	86	100/100	good	good	45	6	0.2
2	3	87	100/100	good	good	60	8	0.2
3	4	85	100/100	good	good	55	7	0.2
4	7	82	100/100	good	good	40	5	0.2
5	9.5	81	100/100	good	good	40	4	0.2
6	4	85	100/100	good	good	45	6	0.2
7	5.5	86	100/100	good	good	20	6	0.01

Effect of this Invention: The aforementioned invention is obtained by mixing a matrix resin and silicon oxide powder at a certain rate which results in a substrate that possesses high water absorption resistance, high adhesion to a dielectric layer and magnetic recording layer. Thus an optical disc with high reliability is obtained.

Moreover, the said procedures resulted in an improvement in the heat resistance that enables an increase in the processing temperature during formation of the thin layer and a decrease in the linear coefficient of expansion. Thus stresses during formation of the inorganic dielectric layer can be limited resulting in improved dimensional precision of the products.

Because the substrate that is obtained with the resin composition explained in this invention possesses hard silicon oxide powder, not only the resistance to damage is improved but also the resistance to solvent during the formation of the resin hard coat layer on the surface is improved. The orientation of the matrix resin is disturbed by the homogenous dispersion of silicone oxide powder thereby limiting the birefringence of the substrate. There are also more physical and optical benefits.